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(54) Title: PROCESS FOR THE FORTIFICATION OF A FRUIT BASED FOOD PRODUCT WITH CALCIUM

(57) Abstract: The present invention relates to a process for the fortification of food products containing fruit, such as fruit juices, concentrates, syrups or spreads with calcium. According to this process an inorganic calcium salt and a calcium salt of all organic acid are added to the fruit containing food product. In particular this method is suitable for food products with fruit containing anthocyanins, such as cranberries. A preferred combination of calcium salts is a calcium salt of lactic acid with calcium chloride.

PROCESS FOR THE FORTIFICATION OF A FRUIT BASED FOOD PRODUCT WITH CALCIUM

- 5 The present invention relates to a process for the fortification of food products containing fruit such as fruit juices, concentrates, syrups or spreads with calcium. Such processes are known from the prior art. In WO 00/28838 a calcium fortified juice based nutritional beverage is described containing depectinized fruit juice and a source of calcium selected from natural milk mineral, calcium lactate gluconate or mixtures thereof. The
- 10 beverage can further contain nutrients such as vitamins. In EP 397 232 also a nutritional beverage containing fruit juice is described wherein as a calcium source calcium chloride, calcium carbonate or calcium-citrate-malate is used.
- US 6,086,927 describes a process for preparing a calcium enriched food product by subsequently mixing in water or fruit juice of calcium hydroxide, a phosphorus based acid,
- 15 calcium lactate and calcium phosphate. The mixture comprises about 40 wt. % of total calcium derived from calcium hydroxide, about 15 wt. % of total calcium derived from calcium lactate and about 45 wt. % of total calcium derived from calcium phosphate.
- 20 The problem which arises when calcium compounds are added to fruit based food products is that colour changes can occur, in particular in case of juices or concentrates obtained from fruit containing pH sensitive colour pigments such as for instance anthocyanins. Anthocyanins are stable at low pH. At higher pH a discolouration from red or blue to brown occurs. This is undesirable. Besides colour stability it is required that the fortified products
- 25 have a stable and acceptable flavour.
- The object of the invention is to provide a process for the fortification of food products containing fruit with calcium such that the colour and preferably also the flavour of the food product is acceptable and remains stable over a longer period of time.
- 30 The invention thus provides a process for fortifying food products containing fruit with calcium, comprising adding to the food product an inorganic calcium salt and a calcium salt of an organic acid. Preferably, at least 20 wt. % of total calcium added is supplied by the organic calcium salt, more preferably at least 50 wt. % of total calcium added is supplied by
- 35 the organic calcium salt. It was found that when at least 20 wt. % of the total calcium is supplied by organic calcium salt a good taste of the food product may be ensured.
- The calcium salt of an organic acid is preferably selected from calcium salts of suitable food grade carboxylic acids, in particular lactic acid, gluconic acid, citric acid, malic acid, fumaric acid, tartaric acid, adipic acid or mixtures thereof, most preferably lactic acid. Examples of these calcium salts are calcium lactate, calcium gluconate, calcium citrate (monocalcium citrate, dicalcium citrate, tricalcium citrate, sodium calcium citrate, potassium calcium citrate,

ammonium calcium citrate), calcium citrate/malate, calcium malate, calcium amino acid chelates and calcium fumarate.

The calcium salt of organic acid can also be obtained by in situ formation by addition of the organic acid or a potassium, sodium and/or ammonium salt thereof and calcium hydroxide, organic acid or a potassium, sodium and/or ammonium salt thereof and calcium hydroxide,

5 calcium hydrate and/or calcium carbonate to the food product.

The inorganic calcium salt is preferably selected from calcium chloride, calcium phosphate (monocalcium phosphate, dicalcium phosphate, tricalcium phosphate, sodium calcium phosphate, potassium calcium phosphate, ammonium calcium phosphate), calcium sulfate, calcium hydroxide, calcium hydrate, calcium carbonate and mixtures thereof, preferably

10 calcium chloride, calcium phosphate or calcium sulfate, most preferably calcium chloride. It should be noted that if the calcium salt of organic acid is formed in situ, the inorganic calcium salt is selected from calcium chloride, calciumphosphate or calcium sulfate.

When the inorganic calcium salt is calcium chloride or calcium phosphate, it can also be obtained by in situ formation, by addition of calcium hydroxide, calcium hydrate and/or

15 calcium carbonate in combination with phosphoric acid or a potassium, sodium and/or ammonium salt thereof and/or hydrochloric acid.

Preferably, at least 20 wt. % of total calcium added is supplied by the inorganic calcium salt. It was found that when at least 20 wt. % of the total calcium is supplied by inorganic calcium

20 salt a good colour stability of the food product may be ensured.

Thus, most preferably 20-80 wt.% of total calcium is supplied by the inorganic acid salt and 20-80 wt% of total calcium is supplied by the organic calcim salt, preferably calcium lactate.

25 As a source for inorganic calcium salts also nature derived calcium sources can be used such as milk calcium, sea weed calcium or calcium obtained from shelves. These products contain for example calcium carbonate or calcium phosphate.

According to a further aspect the invention relates to a process as described above wherein 30 the inorganic calcium salt is a calcium phosphate selected from mono calcium phosphate, dicalcium phosphate, tricalcium phosphate, sodium calcium phosphate, potassium calcium phosphate, ammonium calcium phosphate and the amount of calcium supplied by the calcium phosphate is 15 to 100 %. These salts can also be formed in situ, as described above.

35 The invention also relates to the calcium enriched food product obtained with the process described above, which contains an added inorganic calcium salt and an added calcium salt of an organic acid, wherein preferably at least 20 wt.% of total added calcium is supplied by the organic calcium salt. Preferably the product contains 50 to 80 wt. % of total added calcium of calcium lactate and 20 to 50 wt. % of total added calcium of calcium chloride. With 40 added calcium is meant the calcium which is not naturally present in one of the raw materials of the food product. This means for instance that when the food product contains milk, the milk calcium already present in the milk is not included in the balance of total added calcium.

The food product containing fruit of the invention includes not only juices, but also fruit concentrates, fruit based beverages, nectars, syrups etc. containing fruit. food products can also be spreads, which includes spreadable fruit products such as jams, marmalades and fruit fillings.

The process of the invention is particularly suitable for food products based on fruit containing anthocyanins, such as blueberries, bilberries, cranberries, elderberries, strawberries, raspberries, blackberries) blackcurrants, red, black and blue grapes, plums and cherries.

10

The product obtained after fortification with calcium has a pH lower than 4.5, preferably lower than 3.5, in particular between 2.5 and 3.5.

The calcium concentration in the final product after fortification is determined by the recommended values for daily food intake, but is in particular less than 3000 ppm, preferably less than 600 ppm. A suitable calcium concentration in the juice or spread is 400 to 900 ppm.

EXAMPLES

20 Example 1

Orange juice and apple juice were fortified with 1200 ppm calcium. Calcium phosphate and calcium lactate were added in various ratios. After 5 days at 40 °C the colour, pH and taste were analysed. The results are compiled in TABLES 2 and 3.

25

TABLE 2 Orange juice fortified with calcium lactate/calcium phosphate

Ratio % Calcium from lactate/phosphate	pH	Colour stability	taste
blank	3.73	good	good
100:0	3.84	good	good
75:25	3.78	good	good
50:50	3.71	Good	good
25:75	3.63	Good	good
0:100	3.53	Good	bitter

TABLE 3 Apple juice fortified with calcium lactate/calcium phosphate

Ratio % Calcium from lactate/ phosphate	pH	Colour stability	taste
blank	3.50	good	good
100:0	3.86	good	good
75:25	3.78	good	good
50:50*	3.69	good	good
25:75*	3.58	good	good
0:100*	3.44	good	bitter

*) a precipitation was present

5 Table 2 and 3 show that when more than 75 wt% of the calcium originates from calcium phosphate, the taste is detrimentally affected. Thus with at least 20 wt.% of the calcium added originating from calcium lactate ensures a good taste. The same tests were performed with calcium lactate/calcium citrate blends with the same results.

10

Example 2

15 Cranberry juice was fortified with 500 ppm. First calcium lactate was added to the juice and stirred until all was dissolved. Thereafter calcium chloride was added. The pH was measured and the flavor was assessed. The juices were then stored at 35 °C for 40 hours to check colour stability.

In Table 1 results of this experiment are shown:

20

Table 1

Calcium of calcium lactate (ppm)	Calcium of calcium chloride (ppm)	pH	Colour stability	taste
0	0	2.67		
0	500	2.53	very light, watery	chlorine/bitter

100	400	2.62	good	chlorine/bitter
200	300	2.71	Good	chlorine/bitter
300	200	2.80	Good	good
400	100	2.91	Good	good
500	0	3.00	light/ brownish	tart/astringent

These results show that a good colour stability is ensured with at least 20 wt.% of the calcium supplied originating from the inorganic acid calcium salt, whereas a good taste is ensured with at least 20 wt.% of the calcium originating from the organic acid calcium salt.

5

Example 3

10 Lemonade syrup (Orange form ex Karvan Cevitam) was fortified with a blend of calcium lactate/calcium chloride (dosing level 20 % RDI preserving of 250 ml. The results on pH and taste are compiled in TABLE 4.

TABLE 3 Lemonade syrup juice fortified with calcium lactate/calcium chloride

Ratio % Calcium from lactate/ chloride	pH	taste
blank	3.21	good
100:0	2.96	good
75:25	3.39	good
50:50	3.62	good
25:75	3.79	Little chloride off flavour
0:100	3.91	Chlorine off flavour→ not acceptable

15 These results show that also in lemonade syrups a combination of calcium lactate and an inorganic calcium salt is necessary to obtain acceptable flavour. A good taste is ensured with at least 20 wt.% of the calcium supplied by the organic acid calcium salt.

Example 4

5 Drink yoghurt was fortified (675ppm) with a blend of calcium lactate and mono calcium citrate. When at least 20 wt.% of the calcium supplied originated from calcium lactate a good taste was ensured.

Claims

1. Process for fortifying a food product containing fruit with calcium, comprising adding to the food product an inorganic calcium salt and a calcium salt of an organic acid.

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2. Process according to claim 1 wherein at least 20 wt. % of total calcium added is supplied by the organic calcium salt.

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3. Process according to claim 2 wherein the organic calcium salt is calcium lactate.

4. Process according to claim 1, wherein at least 20 wt.% of total calcium added is supplied by the inorganic calcium salt.

15

5. Process according to claim 1 wherein 20 to 80 wt.% of total calcium added is supplied by the organic calcium salt and 20 to 80 wt. % is supplied by the inorganic calcium salt.

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6. Process according to claim 1, wherein the fruit in the food product is a fruit containing pH sensitive colour pigments.

25

7. Process according to claim 6, wherein the fruit in the food product is a fruit containing anthocyanins.

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8. Process according to claim 7, wherein the fruit is selected from blueberries, bilberries, cranberries, elderberries, strawberries, raspberries, blackberries, blackcurrants, red, black and blue grapes, plums and cherries.

30

9. Process according to claim 8, wherein the fruit is cranberries.

30

10. Process according to claim 1, wherein the calcium salt of an organic acid is selected from calcium salts of lactic acid, gluconic acid, citric acid, malic acid, fumaric acid, tartaric acid, adipic acid and mixtures thereof.

35

11. Process according to claim 1, wherein the calcium salt of organic acid is formed in situ in the food product by the addition to the food product of the organic acid or a potassium, sodium or ammonium salt thereof and calcium hydroxide, calcium hydrate or calcium carbonate.

40

12. Process according to claim 10, wherein the calcium salt of an organic acid is a calcium salt of lactic acid.

13. Process according to claim 1, wherein the inorganic calcium salt is selected from calcium chloride, calcium phosphate, calcium sulphate, Calcium hydrate, calcium carbonate and mixtures thereof.
- 5 14. Process according to claim 1, wherein the inorganic calcium salt is formed in situ in the food product by addition to the food product of calcium hydroxide, calcium hydrate and/or calcium carbonate and phosphoric acid and/or hydrochloric acid or potassium, sodium or ammonium salt thereof.
- 10 15. Process according to claim 11, wherein the inorganic calcium salt is calcium chloride.
16. Process according to claim 1, wherein the food product after fortification with calcium has a pH lower than 4.5.
- 15 17. Process according to claim 14, wherein the food product after fortification with Calcium has a pH lower than 3.5.
18. Process according to claim 1, wherein the calcium concentration in the food product after fortification is less than 3000 ppm.
- 20 19. Process according to claim 16, wherein the calcium concentration in the food product after fortification is less than 600 ppm.
- 25 20. Process according to claim 1, wherein the inorganic calcium salt is a calcium phosphate selected from mono calcium phosphate, dicalcium phosphate, tricalcium phosphate, sodium calcium phosphate, potassium calcium phosphate, ammonium calcium phosphate .
- 30 21. Calcium enriched food product containing fruit, containing an added inorganic calcium salt and an added calcium salt of an organic acid, wherein at least 20 wt. % of total calcium added is supplied by the organic calcium salt.
- 35 22. Calcium enriched food product according to claim 20 wherein the organic calcium salt is calcium lactate.
23. Calcium enriched food product according to claim 21, containing at 50 to 80 wt.% of total calcium added of calcium lactate and 10 to 50 wt. % of total calcium added of calcium chloride.
- 40 24. Calcium enriched food product according to claim 18, which is a juice, concentrate, beverage, syrup, nectar or spread.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER					
IPC 7	A23L2/02	A23L2/52	A23L1/30	A23L1/06	A23L1/10
	A23L1/304				

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 740 380 A (MELACHOURIS NICHOLAS ET AL) 26 April 1988 (1988-04-26) column 2, line 46 -column 4, line 38; examples 3,6 ---	1-24
X	US 4 871 554 A (KALALA ROSE H ET AL) 3 October 1989 (1989-10-03) column 4, line 49 -column 6, line 5; claims; tables I,III,IV,V ---	1-24
X	WO 97 30601 A (PARKER DAVID MYATT ;SMITHKLINE BEECHAM PLC (GB)) 28 August 1997 (1997-08-28) page 3, line 27 -page 5, line 16; example 1 --- ---	1-24
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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PCT/NL 02/00597

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 01799 A (NESTLE SA ;HUTT LIBBY (US); VERSTRATE JOHN (US)) 11 January 2001 (2001-01-11) page 3, line 6 - line 12 page 3, line 33 -page 4, line 11; claims 1,6,8; example ---	1-24
Y	US 4 919 963 A (HECKERT DAVID C) 24 April 1990 (1990-04-24) column 8, line 17 -column 9, line 22 ---	1-24
Y	US 6 086 927 A (FRIELICH SEAN H ET AL) 11 July 2000 (2000-07-11) cited in the application claims 1,6,23,24,31 -----	1-24

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/NL 02/00597

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 4740380	A	26-04-1988	NONE		
US 4871554	A	03-10-1989	CA	1323793 A1	02-11-1993
WO 9730601	A	28-08-1997	AU	719631 B2	11-05-2000
			AU	1872597 A	10-09-1997
			BG	102702 A	30-04-1999
			BR	9707618 A	27-07-1999
			CA	2247114 A1	28-08-1997
			CH	690815 A5	31-01-2001
			CN	1211166 A	17-03-1999
			CZ	9802653 A3	13-01-1999
			DE	19781601 T0	15-04-1999
			EA	1375 B1	26-02-2001
			WO	9730601 A1	28-08-1997
			EP	0874558 A1	04-11-1998
			FI	981781 A	19-08-1998
			GB	2326596 A , B	30-12-1998
			HU	9900998 A2	28-07-1999
			JP	11507842 T	13-07-1999
			LU	90276 A2	28-10-1998
			NO	983798 A	07-10-1998
			NZ	331363 A	27-03-2000
			PL	328472 A1	01-02-1999
			SE	9802763 A	03-09-1998
			SI	9720017 A , B	30-06-1999
			SK	112898 A3	11-02-1999
			TR	9801623 T2	23-11-1998
			US	6319490 B1	20-11-2001
			US	2001043908 A1	22-11-2001
			US	2002044992 A1	18-04-2002
			ZA	9701358 A	18-02-1998
WO 0101799	A	11-01-2001	AU	6689300 A	22-01-2001
			WO	0101799 A1	11-01-2001
			EP	1198182 A1	24-04-2002
			US	2002132034 A1	19-09-2002
US 4919963	A	24-04-1990	US	4722847 A	02-02-1988
			AT	55042 T	15-08-1990
			AU	594271 B2	01-03-1990
			AU	7253387 A	12-11-1987
			CA	1325130 A1	14-12-1993
			DE	3764017 D1	06-09-1990
			DE	244903 T1	07-04-1988
			EG	18049 A	30-08-1991
			EP	0244903 A1	11-11-1987
			ES	2016336 T5	16-11-1999
			FI	872007 A , B,	08-11-1987
			GR	3000729 T3	10-10-1991
			GR	3031471 T3	31-01-2000
			IE	60333 B	29-06-1994
			JP	2559732 B2	04-12-1996
			JP	63052864 A	07-03-1988
			KR	9604263 B1	30-03-1996
			MX	165456 B	11-11-1992
			PH	23972 A	23-01-1990
			PH	27164 A	02-04-1993

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/NL 02/00597

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4919963	A	PT 84820 A ,B TR 24771 A	01-06-1987 09-03-1992
US 6086927	A	11-07-2000	NONE

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